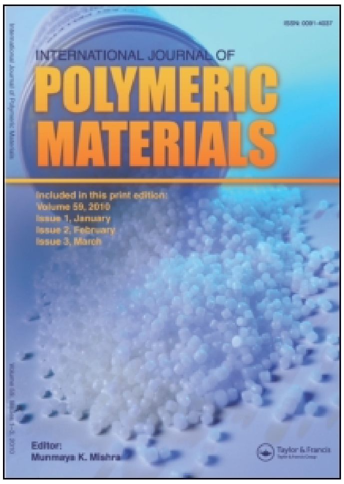

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Thermal and NMR Studies of Polystyrene Blends

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The effect of addition of poly (propylene oxide) (PPO) and polystyrene with low molecular weight (LPS) to polystyrene (PS) was investigated blending these polymers in a Haake internal mixer. The PPO and LPS range was established up to 10% by weight. The blends were analysed by differential scanning calorimetry (DSC) and carbon-13 nuclear magnetic resonance spectroscopy at solid state (NMR), using conventional NMR techniques as cross-polarisation/magic angle spinning (CP/MAS) and proton spin-lattice relaxation time in the rotating frame ($T_1{}^H\rho$). The addition of 1 and 5% of PPO and 5% of LPS to PS made the blends of PS/PPO and PS/LPS more rigid.

Keywords: Blends; polystyrene; poly(propylene oxide); plasticization effect

INTRODUCTION

Polymer blends is one of the most important class of polymer science, because it allows the tailoring of new materials with specific features. Therefore, they have been subject of important researches. In the case of an amorphous polymer blends it is possible to achieve subtle modification on final properties as an improvement to the polymer processability at low cost. The development of new polymer blends is complex due to thermodynamics and their processing conditions [1, 2].

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Polystyrene (PS) is one of the most used thermoplastics, however, its processability is difficult. To improve it an addition of other polymer with low molecular weight as PPO was done and the plasticization effects could be observed [3]. This same blend when obtained by solvent cast technique was analysed by X-ray photoelectron spectroscopy and it showed that the surface behaviour is strongly dependent on the solvent used. Despite the much lower surface tension of PPO compared to PS, no surface segregation of PPO was observed in the PPO/PS blends cast from tetrahydrofuran while the blends cast from chloroform exhibits a higher surface enrichment of PPO [4].

To extract further information on the PS/PPO and PS/LPS systems related to the molecular dynamic, solid state NMR spectroscopy was chosen. As it is known the comparison between MAS (using special conditions to detect only the mobile regions) and CP/MAS is a first indication of molecular mobility and heterogeneity. The variable contact-time experiment permits to obtain responses from the distribution form of the carbon-13 CP/MAS spectra decay and it is also possible to measure the proton $T_1\rho$. As this parameter has been influenced by spin-spin communication; if it is not efficient, two or more domains can be detected, as a consequence of sample heterogeneity. But the changes in the value of this parameter, for example, a decrease in the value of proton $T_1\rho$, can be attributed to the strong interaction between polymer blends components [5–9]. On the other hand, an increase can be related to a plasticization effects [10–12].

The main purpose of this work was to investigate the mobility of the PS and their blends with PPO and LPS, using thermal and NMR measurements.

EXPERIMENTAL

Materials

Table I shows the characterisation of the homopolymers used in this work.

PS and LPS were kindly supplied by EDN-Poliestireno do Sul Ltda and EDN-Estireno do Nordeste Ltda., respectively, PPO was supplied by Dow Química S.A.

TABLE I Characteristics of the homopolymers

Polymer	*Mn*	*Mw/Mn*
PS	110,895	2.63
LPS	4,526	4.81
PPO	896*	1.07

Calculated by gel permeation chromatography (GPC)
*Calculated by vapour pressure osmometry (VPO).

Blends Preparation

The blends were prepared in a mixing chamber using a HAAKE internal Rheocord 600 at 160°C for 10 minutes and the rotation speed was approximately 150 ppm. The amount of PPO and LPS was changed from 1 to 10% (wt/wt).

Thermal Analysis

Perkin Elmer DSC-7 differential scanning calorimetry was used to determinate the value of the glass transition temperature (*Tg*) for all the blends. The operational conditions used were: heat rate 10°C/min and the temperature range was – 25 – 150°C.

NMR Measurements

Solid state carbon-13 NMR techniques were performed on a VARIAN VXR 300 spectrometer, at room temperature. The hydrogen resonance frequency was 300 MHz and the carbon-13 resonance frequency was 75.4 MHz. The Hartman-Hahn CP matching and dipolar decoupling field was ~40 kHz, and the delay was 2s. The contact time varied from 200 to 8,000 μs, and the MAS rate was 5 kHz. The $T_1{}^H\rho$ were obtained from the carbon-13 CP/MAS intensity decay with increasing contact-time. Carbon-13 spectra were referenced to the chemical shift of the methyl group of the hexamethyl benzene (17.3 ppm).

RESULTS AND DISCUSSION

Thermal Analysis

Table II presents the changes in *Tg* according to the amount of PPO or LPS added in the PS matrix. The results presented a decrease in the *Tg*

TABLE II Dependence of *Tg* with the amount of PPO and LPS added

Polymer content in the blends wt %	*Tg values (°C)* *PPO*	*LPS*
1	101	101
5	89	101
10	77	100

values with an increase in the PPO amount when compared with pure PS processed at the same conditions of the blends, as a consequence of the plasticization effect of PPO. Therefore, this behaviour was not observed when LPS was added to PS. The addition of LPS did not change the *Tg* values for all compositions studied.

NMR Analysis

From the carbon-13 CP/MAS NMR spectra of PS and PS/PPO blends was verified that the addition of small amounts of PPO (1 – 5%) caused a decrease in the mobility of the blends when compared with PS.

The molecular mobility of the PS/PPO and PS/LPS blends were careful analysed by the values of $T_1^H\rho$, obtained from the plot of carbon-13 peak intensities *versus* contact-times, where the range of contact-time varied from short to long contact-times. Table III illustrates the $T_1^H\rho$ values for PS and their blends with PPO, for three different types of carbon. The addition of small amount of PPO (1%) caused a decrease on the system mobility, which was not detected from DSC results, due to the measurement scale. It can also be observed a significant decrease in blend mobility when 5% of PPO was added and compared with 1% of PPO. This fact could be explained considering that PPO plasticizes the PS initially, changing the chain ordinations.

The behaviour of PS/LPS blends focused by $T_1^H\rho$ values are showed in Table IV.

TABLE III $T_1^H\rho$ values for the carbon-13 located on 146.8 ppm for PS/PPO blends

Sample	$T_1^H\rho$ *(ms)*
PS processed	6.3
PS/PPO 99/1	4.7
PS/PPO 95/5	2.7

TABLE IV $T_1{}^H\rho$ values for the carbon-13 located on 146.8 ppm for PS/LPS blends

Sample	$T_1{}^H\rho(ms)$
PS processed	6.3
LPS	2.5
PS/LPS 99/1	4.8
PS/LPS 95/5	1.9
PS/LPS 90/10	5.0

From the data of Table IV, it can be observed that the addition of 1% of LPS cause the same effect on the $T_1{}^H\rho$ relaxation parameter. Comparing the 5% of each polymer the LPS cause a higher decrease in this parameter in relation to the PPO. This behaviour can be explained due to the fact that LPS present higher interaction with PS than the PPO. Analysing the effect caused by 10% of LPS added to PS it can be characterised as an improvement of the blend mobility; as a consequence of changes in the molecular packing caused by LPS, which can be promoting the formation of rigid sites with concentrated tension, where crazes can rapidly be formed on the material interface.

CONCLUSION

From the NMR data it can be seen that LPS was much more effective as a plasticizer for PS than PPO. The blends with LPS also presented a different behaviour in relation to the molecular mobility.

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